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## (54) USE OF 1,3-DITHIOLANE-2-THIONE ADDITIVES FOR LUBRICANTS

VERWENDUNG VON 1,3-DITHIOLAN-2-THON-ADDITIVE FÜR SCHMIERSTOFFE

UTILISATION D'ADDITIFS DERIVES DE 1,3-DITHIOLANE-2-THIONE POUR LUBRIFIANTS

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**Description**

## BACKGROUND OF THE INVENTION

5      **1. Field of the Invention**

**[0001]** The present invention is related to the use of 1,3-dithiolane-2-thione additives in lubricants, especially lubricating oils, and, more particularly, to improve the anti-corrosion, characteristics.

10     **2. Description of Related Art**

**[0002]** In developing lubricating oils, there have been many attempts to provide additives that impart anti-fatigue, anti-wear, and extreme pressure properties thereto. Zinc dialkyldithiophosphates (ZDDP) have been used in formulated oils as anti-wear additives for more than 50 years. However, zinc dialkyldithiophosphates give rise to ash, which contributes to particulate matter in automotive exhaust emissions, and regulatory agencies are seeking to reduce emissions of zinc into the environment. In addition, phosphorus, also a component of ZDDP, is suspected of limiting the service life of the catalytic converters that are used on cars to reduce pollution. It is important to limit the particulate matter and pollution formed during engine use for toxicological and environmental reasons, but it is also important to maintain undiminished the anti-wear properties of the lubricating oil.

20     **[0003]** In view of the aforementioned shortcomings of the known zinc and phosphorus-containing additives, efforts have been made to provide lubricating oil additives that contain neither zinc nor phosphorus or, at least, contain them in substantially reduced amounts. Illustrative of non-zinc, i.e., ashless, non-phosphorus-containing lubricating oil additives are the reaction products of 2,5-dimercapto-1,3,4-thiadiazoles and unsaturated mono-, di-, and tri-glycerides disclosed in U.S. Patent No. 5,512,190 and the dialkyl dithiocarbamate-derived organic ethers of U.S. Patent No. 5,514,189.

25     **[0004]** U.S. Patent No. 5,512,190 discloses an additive that provides anti-wear properties to a lubricating oil. The additive is the reaction product of 2,5-dimercapto-1,3,4-thiadiazole and a mixture of unsaturated mono-, di-, and triglycerides. Also disclosed is a lubricating oil additive with anti-wear properties produced by reacting a mixture of unsaturated mono-, di-, and triglycerides with diethanolamine to provide an intermediate reaction product and reacting the intermediate reaction product with 2,5-dimercapto-1,3,4 thiadiazole.

30     **[0005]** U.S. Patent No. 5,514,189 discloses that dialkyl dithiocarbamate-derived organic ethers have been found to be effective anti-wear/antioxidant additives for lubricants and fuels.

**[0006]** U.S. Patent No. 2,440,991 discloses the use of acyclic trithiocarbonates that are S,S' disubstituted with carboxylic acids of 16 to 18 carbons. These compounds are said to be useful as rust inhibitors for lubricants.

35     **[0007]** U.S. Patent No. 2,498,936 discloses the use of acyclic trithiocarbonates as extreme pressure additives. These additives are prepared by the reaction of the salts of a trithiocarbonate with an alkyl dihalide. The use of alkyl halides in the preparation of lubricant additives is now environmentally undesirable, as this may tend to increase the levels of halogen present in the finished additive.

**[0008]** U.S. Patent No. 3,166,580 discloses the preparation of dicyclopentyltrithiocarbonate from alkali metal trithiocarbonates and cyclopentyl halides, and the use of the resulting product as "lubricating additives".

40     **[0009]** U.S. Patent No. 3,481,871 discloses organo-sulfur derivatives that are produced by reacting a mercaptan with a sulfur chloride compound, reacting the resulting organic organic sulfenyl or thiosulfenyl chloride with an olefin, and finally reacting the resulting product with a metal sulfur-containing salt. The final product may be used in lubricating oils and other industrial fluids as a load-carrying additive.

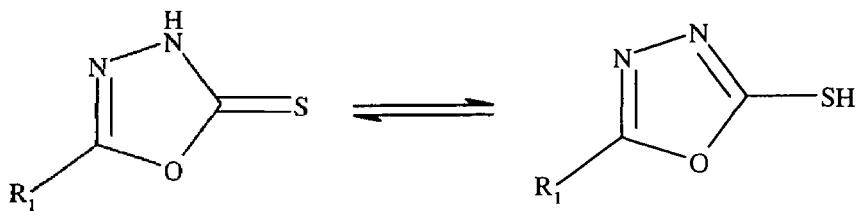
45     **[0010]** U.S. Patent No. 4,908,142 discloses additives containing a salt or complex of trithiocarbonic acid that are said to be useful in lubricants to enhance the extreme pressure/anti-wear and anti-oxidation capabilities thereof. The lubricants are preferably oils of lubricating viscosity, which may be thickened to a grease-like consistency with one or more oil thickeners, and contain from about 0.1 to about 20 weight percent of said additives.

**[0011]** U.S. Patent Nos. 5,084,195 and 5,300,243 disclose N-acyl-thiourethane thioureas as anti-wear additives specified for lubricants or hydraulic fluids.

50     **[0012]** U.S. Patent No. 6,551,966 discloses a composition comprising:

- (A) a lubricant, and
- (B) at least one 5-alkyl-2-mercaptop-1,3,4-oxadiazole compound of the formula:

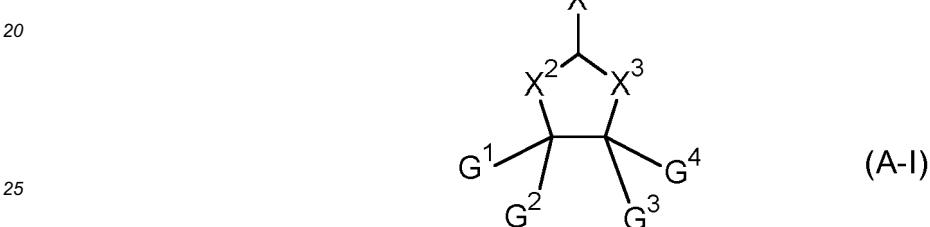
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wherein R 1 is a hydrocarbon or functionalized hydrocarbon of from 1 to 30 carbon atoms. Soviet Patent Nos. SU 1,447,818; SU 1,439,098; SU 1,425,191; SU 1,361,142; SU 1,351,924; SU 1,268,573; and SU 1,082,784 describe the use of acyclic S-alkyl, S-alkyl' disubstituted trithiocarbonates as multifunctional additives for lubricants, particularly anti-scuffing agents.

[0013] JP 46,037,176 discloses the use of the unsubstituted compound 1,3-dithiolane-2-thione as a non-corrosive extreme pressure agent for lubricants.

[0014] EP-A 0 825 246 discloses heterocyclic compounds of the formula



Wherein in Formula (A-I): X<sup>1</sup>, X<sup>2</sup> and X<sup>3</sup> are independently O or S, and X<sup>2</sup> and X<sup>3</sup> can be NR<sup>1</sup> wherein R<sup>1</sup> is hydrogen or hydrocarbyl; and G<sup>1</sup>, G<sup>2</sup>, G<sup>3</sup> and G<sup>4</sup> are independently R<sup>2</sup>, OR<sup>2</sup> or R<sup>3</sup>OR<sup>2</sup>, wherein R<sup>2</sup> is hydrogen or hydrocarbyl and R<sup>3</sup> is hydrocarbylene or hydrocarbylidene.

## SUMMARY OF THE INVENTION

[0015] It has now been found that substituted 1,3-dithiolane-2-thiones, which are trithiocarbonates contained within a five membered ring, are useful as lubricant additives, imparting anti-wear and anti-corrosive properties to the lubricant. The presence of properly chosen substituents can impart improved solubility of the additive in the lubricant. These substituted 1,3-dithiolane-2-thiones can be conveniently prepared by reaction of an alkali metal xanthate with an appropriate oxirane (epoxide), and can be used either alone or in synergistic combination with a zinc dihydrocarbyldithiophosphate or an ashless phosphorus- containing additive, such as trilauryl phosphate or triphenyl phosphate.

[0016] The present invention is directed to additives that can be used as either partial or complete replacements for the zinc dialkyldithiophosphates currently used. They can also be used in combination with other additives typically found in motor oils, as well as other ashless anti-wear additives. The typical additives found in motor oils include dispersants, detergents, anti-wear agents, extreme pressure agents, rust inhibitors, antioxidants, antifoamants, friction modifiers, Viscosity Index (V.I.) improvers, metal passivators, and pour point depressants.

[0017] The compounds employed in the practice of the present invention are substituted 1,3-dithiolane-2-thiones that can be used as non-phosphorus-containing, anti-corrosion, and also anti-fatigue, anti-wear, extreme pressure additives for fuels and lubricating oils.

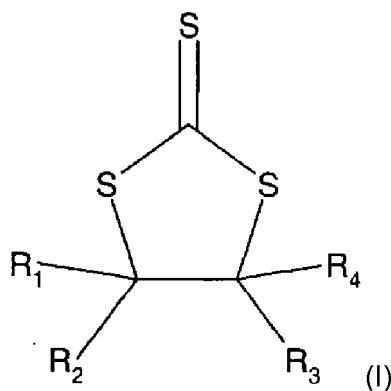
[0018] The present invention also relates to the use of at least one substituted 1,3-dithiolane-2-thione in lubricating oil compositions.

[0019] It is an object of the present invention to provide a new use for substituted 1,3-dithiolane-2-thiones, useful either alone or in combination with other lubricant additives.

[0020] The additives of the present invention are especially useful as components in many different lubricating oil compositions to improve the anti-corrosion properties. The additives can be included in a variety of oils with lubricating viscosity including natural and synthetic lubricating oils and mixtures thereof.

[0021] The additives can be included in crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines. The compositions can also be used in gas engine lubricants, turbine lubricants, automatic transmission fluids, gear lubricants, compressor lubricants, metal-working lubricants, hydraulic fluids, and other lubricating oil and grease compositions.

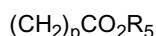
[0022] The used substituted 1,3-dithiolane-2-thiones has the following generic formula (I):



wherein:

20  $R_1$  is a carboxy alkyl

of the structure:



25 wherein:

25  $p$  is from 1 to 50, and

30  $R_5$  is selected from the group consisting of chain-substituted saturated hydrocarbyl;

35  $R_2$ ,  $R_3$ , and  $R_4$  are independently selected from the group consisting of hydrogen and alkyl;

wherein said alkyl groups are unsubstituted or substituted with 1,3-dithiolane-2-thione.

[0023] As employed herein, the term "hydrocarbyl" includes hydrocarbon as well as substantially hydrocarbon groups. "Substantially hydrocarbon" describes groups that contain heteroatom substituents that do not alter the predominantly hydrocarbon nature of the group. Examples of hydrocarbyl groups include the following:

40 (A) hydrocarbon substituents, i.e., aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, aromatic substituents, aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, and the like, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (that is, for example, any two indicated substituents may together form an alicyclic radical);

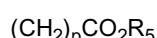
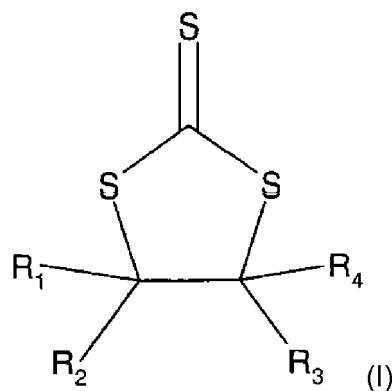
45 (B) substituted hydrocarbon substituents, i.e., those substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent; those skilled in the art will be aware of such groups (e.g., halo, hydroxy, mercapto, nitro, nitroso, sulfoxyl, etc.);

50 (C) heteroatom substituents, i.e., substituents that will, while having a predominantly hydrocarbon character within the context of this invention, contain an atom other than carbon present in a ring or chain otherwise composed of carbon atoms (e.g., alkoxy or alkylthio). Suitable heteroatoms will be apparent to those of ordinary skill in the art and include, for example, sulfur, oxygen, nitrogen, and such substituents as, e.g., pyridyl, furyl, thienyl, imidazolyl, etc. Preferably, no more than about 2, more preferably no more than one, hetero substituent will be present for every ten carbon atoms in the hydrocarbyl group. More preferably, there will be no such heteroatom substituents in the hydrocarbyl group, i.e., the hydrocarbyl group is purely hydrocarbon.

[0024] More particularly, the present invention is directed to the use of a composition comprising:

55 (A) a lubricant and

(B) at least one 1,3-dithiolane-2-thione of formula (I):



20 wherein:

p is from 1 to 50, and

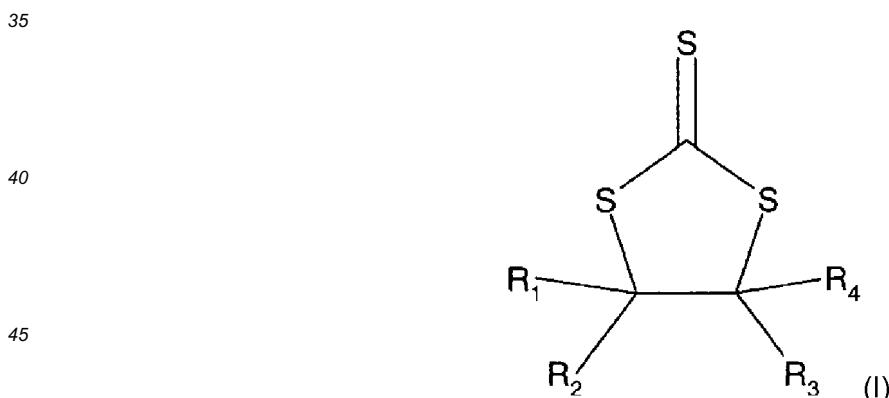
R<sub>5</sub> is selected from the group consisting of chain-substituted saturated hydrocarbyl;

25 R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> are independently selected from the group consisting of hydrogen and alkyl; wherein said alkyl is unsubstituted or substituted with 1,3-dithiolane-2-thione; and, optionally,

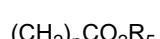
(C) at least one phosphorus-containing additive, for improving the anti-corrosion properties.

30 **DESCRIPTION OF THE PREFERRED EMBODIMENTS**

**[0025]** As stated above, the class of anti-fatigue, anti-wear, and extreme pressure additives can have the following formula (I):



50 R<sub>1</sub> is a carboxy alkyl of the structure:



wherein:

55

p is from 1 to 50, and

R<sub>5</sub> is selected from the group consisting of chain-substituted saturated hydrocarbyl;

R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> are independently selected from the group consisting of hydrogen and alkyl; wherein said alkyl is unsubstituted or substituted with 1,3-dithiolane-2-thione.

5 [0026] Preferably, R<sub>2</sub> is independently selected from the group consisting of:

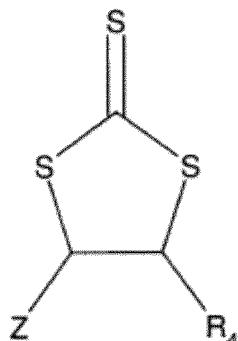
(A) Alkyl groups of from 1 to 50 carbon atoms, including, but not limited to, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, triacontyl, isomers of the foregoing, and the like. By "isomers" such moieties as branched alkyls and cycloalkyls are intended to be included. Examples of such branched alkyls include isopropyl, isobutyl, isopentyl, isoheptyl, isoocetyl, sec-butyl, 1-methylbutyl, 1-ethylpropyl, and the like. Examples of such cycloalkyls include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclooctyl, and the like.

15 [0027] In the formula described above, R<sub>5</sub> is preferably chain-substituted saturated hydrocarbyl. Examples of R<sub>5</sub> include, but are not limited to, straight chain or branched chain alkyl or alkenyl groups containing from one to fifty carbon atoms, including, but not limited to, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, 2-ethyl hexyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, oleyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, triacontyl, isomers of the foregoing, and the like; and cycloalkyl groups, such as cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, and cyclododecyl.

20 [0028] R<sub>1</sub> and R<sub>3</sub> are residues derived from an epoxidized fatty acid ester. Most preferably, R<sub>1</sub> and R<sub>3</sub> are residues derived from an epoxidized 2-ethyl hexyl tallate ester.

25 [0029] Especially preferred substituted cyclic 1,3-dithiolane-2-thione additives for use in the practice of the present invention include those having the following structure:

25



wherein Z is (CH<sub>2</sub>)<sub>p</sub>CO<sub>2</sub>R<sub>3</sub> and the group ZCHCHR<sub>4</sub> is a residue from the reaction of a xanthate with an epoxidized unsaturated acid ester, such as an epoxidized ester of oleic, linoleic, linolenic, or eleostearic acid; or an epoxidized tall oil (tallate) ester, tallate and oleate esters being a preferred embodiment, and reaction products of 2-ethylhexyl tallate being particularly preferred.

40 [0030] The preparation of 1,3-dithiolane-2-thiones from epoxides is described and discussed by Owen, L.N. et al. in J.C.S. Perkin Trans. I, (8) 1975, 748-754, which is incorporated by reference herein.

45 [0031] A class of desirable, oil soluble 1,3-dithiolane-2-thione additives can be prepared by the reaction of an alkali metal xanthate, such as sodium butyl xanthate with an epoxidized  $\alpha$ -olefin, such as epoxy dodecane or epoxy tetradecane, or mixtures thereof. These compounds are articles of commerce, available under the Vikolox® trademark from Arkema.

50 [0032] A particularly desirable, liquid, oil soluble 1,3-dithiolane-2-thione additive can be prepared by the reaction of a sodium xanthate with epoxidized 2-ethylhexyl tallate, which is an article of commerce available as Drapex® 4.4 from Crompton Corporation.

55 [0033] Suitable epoxides for use in the preparation of the 1,3-dithiolane-2-thiones employed in the practice of the present invention include epoxidized C<sub>1</sub>-C<sub>18</sub> esters of unsaturated C<sub>3</sub>-C<sub>36</sub> carboxylic acids, particularly epoxidized esters of C<sub>12</sub>-C<sub>20</sub> acids, such as epoxidized methyl tallate, epoxidized butyl tallate, epoxidized 2-ethylhexyl tallate, epoxidized octyl tallate, and epoxidized methyl oleate, epoxidized butyl oleate, epoxidized 2-ethylhexyl oleate, epoxidized octyl oleate, and the like; epoxidized unsaturated oils, such as epoxidized soybean oil, epoxidized canola oil, and the like.

[0034] The use of the 1,3-dithiolane-2-thiones of this invention can improve the anti-corrosion, anti-fatigue, anti-wear, and extreme pressure properties of a lubricant.

[0035] The substituted 1,3-dithiolane-2-thione additives can be used as either a partial or complete replacement for the zinc dialkyldithiophosphates currently used. The 1,3-dithiolane-2-thiones can be used either alone or in synergistic

combination with (1) zinc dihydrocarbyldithiophosphates or (2) ashless phosphorus-containing additives or (3) mixtures of (1) and (2), in order to reduce the amounts of zinc and phosphorus that are currently used, without diminishing anti-wear performance. They can also be used in combination with other additives typically found in lubricating oils, as well as with other antiwear additives. The additives typically found in lubricating oils are, for example, dispersants, detergents, corrosion/rust inhibitors, antioxidants, anti-wear agents, antifoamants, friction modifiers, seal swell agents, demulsifiers, VI improvers, pour point depressants, and the like. See, for example, U.S. Patent No. 5,498,809 for a description of useful lubricating oil composition additives.

[0036] Examples of dispersants include polyisobutylene succinimides, polyisobutylene succinate esters, Mannich Base ashless dispersants, and the like.

[0037] Examples of detergents include metallic and ashless alkyl phenates, metallic and ashless sulfurized alkyl phenates, metallic and ashless alkyl sulfonates, metallic and ashless alkyl salicylates, metallic and ashless saligenin derivatives, and the like.

[0038] Examples of antioxidants include alkylated diphenylamines, N-alkylated phenylenediamines, phenyl- $\alpha$ -naphthylamine, alkylated phenyl- $\alpha$ -naphthylamine, dimethyl quinolines, trimethyldihydroquinolines and oligomeric compositions derived therefrom, hindered phenolics, alkylated hydroquinones, hydroxylated thiadiphenyl ethers, alkylidenebisphenols, thiopropionates, metallic dithiocarbamates, 1,3,4-dimercaptothiadiazole and derivatives, oil soluble copper compounds, and the like.

[0039] The following are exemplary of such additives and are commercially available from Crompton Corporation: Naugalube® 438, Naugalube 438L, Naugalube 640, Naugalube 635, Naugalube 680, Naugalube AMS, Naugalube APAN, Naugard® PANA, Naugalube TMQ, Naugalube 531, Naugalube 431, Naugard BHT, Naugalube 403, and Naugalube 420, among others.

[0040] Examples of anti-wear additives that can be used in combination with the additives include organo-borates, organo-phosphites, organo-phosphates, organic sulfur-containing compounds, sulfurized olefins, sulfurized fatty acid derivatives (esters), chlorinated paraffins, zinc dialkyldithiophosphates, zinc diaryldithiophosphates, dialkyldithiophosphate esters, diaryl dithiophosphate esters, phosphosulfurized hydrocarbons, and the like.

[0041] The following are exemplary of such additives and are commercially available from The Lubrizol Corporation: Lubrizol 677A, Lubrizol 1095, Lubrizol 1097, Lubrizol 1360, Lubrizol 1395, Lubrizol 5139, and Lubrizol 5604, among others; and from Ciba Corporation: Irgalube 353.

[0042] Examples of friction modifiers include fatty acid esters and amides, organo molybdenum compounds, molybdenum dialkyldithiocarbamates, molybdenum dialkyl dithiophosphates, molybdenum disulfide, tri-molybdenum cluster dialkyldithiocarbamates, non-sulfur molybdenum compounds and the like.

[0043] The following are exemplary of molybdenum additives and are commercially available from R. T. Vanderbilt Company, Inc.: Molyvan A, Molyvan L, Molyvan 807, Molyvan 856B, Molyvan 822, Molyvan 855, among others. The following are also exemplary of such additives and are commercially available from Asahi Denka Kogyo K.K.: SAKURA-LUBE 100, SAKURA-LUBE 165, SAKURA-LUBE 300, SAKURA-LUBE 31 OG, SAKURA-LUBE 321, SAKURA-LUBE 474, SAKURA-LUBE 600, SAKURA-LUBE 700, among others. The following are also exemplary of such additives and are commercially available from Akzo Nobel Chemicals GmbH: Ketjen-Ox 77M, Ketjen-Ox 77TS, among others, and from Crompton Corporation: Naugalube MolyFM™ 2543.

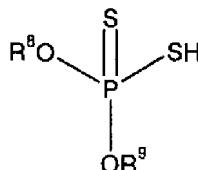
[0044] An example of an anti-foamant is polysiloxane, and the like.

[0045] Examples of rust inhibitors are polyoxyalkylene polyol, benzotriazole derivatives, and the like.

[0046] Examples of VI improvers include olefin copolymers and dispersant olefin copolymers, and the like.

[0047] An example of a pour point depressant is polymethacrylate, and the like.

[0048] As noted above, suitable anti-wear compositions may include dihydrocarbyldithiophosphates. Preferably, the hydrocarbyl groups contain an average of at least 3 carbon atoms. Particularly useful are metal salts of at least one dihydrocarbyl dithiophosphoric acid wherein the hydrocarbyl groups contain an average of at least 3 carbon atoms. The acids from which the dihydrocarbyl dithiophosphates can be derived can be illustrated by acids of the formula:



55 wherein R<sup>8</sup> and R<sup>9</sup> are the same or different and are alkyl, cycloalkyl, aralkyl, alkaryl, or substituted substantially hydrocarbon radical derivatives of any of the above groups, and wherein the R<sup>8</sup> and R<sup>9</sup> groups in the acid each have, on average, at least 3 carbon atoms. By "substantially hydrocarbon" is meant radicals containing atoms or groups, e.g., 1 to 4 substituent groups per radical moiety, such as ether, ester, nitro, halogen, or the like, that do not materially affect

the hydrocarbon character of the radical.

[0049] Specific examples of suitable R<sup>8</sup> and R<sup>9</sup> radicals include isopropyl, isobutyl, n-butyl, sec-butyl, n-hexyl, heptyl, 2-ethylhexyl, diisobutyl, isoctyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, butylphenyl, o,p-dipentylphenyl, octylphenyl, polyisobutene-(molecular weight about 350)-substituted phenyl, tetrapropylene-substituted phenyl,  $\beta$ -octylbutylnaphthyl, cyclopentyl, cyclohexyl, phenyl, chlorophenyl, o-dichlorophenyl, bromophenyl, naphthyl, 2-methylcyclohexyl, benzyl, chlorobenzyl, chloropentyl, dichlorophenyl, nitrophenyl, dichlorodecyl, xenyl, and similar radicals. Alkyl radicals having from about 3 to about 30 carbon atoms and aryl radicals having from about 6 to about 30 carbon atoms are preferred. Particularly preferred R<sup>8</sup> and R<sup>9</sup> radicals are alkyl of from 3 to 12 carbon atoms.

[0050] The phosphorodithioic acids are readily obtainable by the reaction of phosphorus pentasulfide and an alcohol or phenol. The reaction involves mixing, at a temperature of about 20°C to 200°C, 4 moles of the alcohol or phenol with one mole of phosphorus pentasulfide. Hydrogen sulfide is liberated as the reaction takes place. Mixtures of alcohols, phenols, or both can be employed, e.g., mixtures of C<sub>3</sub> to C<sub>30</sub> alcohols, C<sub>6</sub> to C<sub>30</sub> aromatic alcohols, and the like.

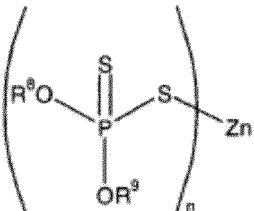
[0051] The metals useful to make the phosphate salts include Group I metals, Group II metals, aluminum, lead, tin, molybdenum, manganese, cobalt, and nickel. Zinc is the preferred metal. Examples of metal compounds that can be reacted with the acid include lithium oxide, lithium hydroxide, lithium carbonate, lithium pentylate, sodium oxide, sodium hydroxide, sodium carbonate, sodium methylate, sodium propylate, sodium phenoxide, potassium oxide, potassium hydroxide, potassium carbonate, potassium methylate, silver oxide, silver carbonate, magnesium oxide, magnesium hydroxide, magnesium carbonate, magnesium ethylate, magnesium propylate, magnesium phenoxide, calcium oxide, calcium hydroxide, calcium carbonate, calcium methylate, calcium propylate, calcium pentylate, zinc oxide, zinc hydroxide, zinc carbonate, zinc propylate, strontium oxide, strontium hydroxide, cadmium oxide, cadmium hydroxide, cadmium carbonate, cadmium ethylate, barium oxide, barium hydroxide, barium hydrate, barium carbonate, barium ethylate, barium pentylate, aluminum oxide, aluminum propylate, lead oxide, lead hydroxide, lead carbonate, tin oxide, tin butylate, cobalt oxide, cobalt hydroxide, cobalt carbonate, cobalt pentylate, nickel oxide, nickel hydroxide, nickel carbonate, and the like. In some instances, the incorporation of certain ingredients, particularly carboxylic acids or metal carboxylates, such as, small amounts of the metal acetate or acetic acid, used in conjunction with the metal reactant will facilitate the reaction and result in an improved product. For example, the use of up to about 5% of zinc acetate in combination with the required amount of zinc oxide facilitates the formation of a zinc phosphorodithioate.

[0052] The preparation of metal phosphorodithioates is well known in the art and is described in a large number of issued patents, including U.S. Patent Nos. 3,293,181; 3,397,145; 3,396,109; and 3,442,804. Also useful as anti-wear additives are amine derivatives of dithiophosphoric acid compounds, such as are described in U.S. Patent No. 3,637,499.

[0053] The zinc salts are most commonly used as anti-wear additives in lubricating oil in amounts of 0.1 to 10, preferably 0.2 to 2, wt. %, based upon the total weight of the lubricating oil composition. They may be prepared in accordance with known techniques by first forming a dithiophosphoric acid, usually by reaction of an alcohol or a phenol with P<sub>2</sub>S<sub>5</sub> and then neutralizing the dithiophosphoric acid with a suitable zinc compound.

[0054] Mixtures of alcohols can be used, including mixtures of primary and secondary alcohols, secondary generally for imparting improved anti-wear properties and primary for thermal stability. In general, any basic or neutral zinc compound could be used, but the oxides, hydroxides, and carbonates are most generally employed. Commercial additives frequently contain an excess of zinc owing to use of an excess of the basic zinc compound in the neutralization reaction.

[0055] The zinc dihydrocarbyl dithiophosphates (ZDDP) are oil soluble salts of dihydrocarbyl esters of dithiophosphoric acids and can be represented by the following formula:



wherein n, R<sup>8</sup>, and R<sup>9</sup> are as described above.

#### 55 Lubricant Compositions used for anti-corrosion

[0056] Compositions, when they contain these additives, are typically blended into a base oil in amounts such that the additives therein are effective to provide their normal attendant functions. Representative effective amounts of such additives are illustrated in TABLE 1.

TABLE 1		
Additives	Preferred Weight%	More Preferred Weight
V.I. Improver	1-12	1-4
Corrosion Inhibitor	0.01-3	0.01-1.5
Oxidation Inhibitor	0.01-5	0.01-1.5
Dispersant	0.1-10	0.1-5
Lube Oil Flow Improver	0.01-2	0.01-1.5
Detergent/Rust Inhibitor	0.01-6	0.01-3
Pour Point Depressant	0.01-1.5	0.01-0.5
Anti-foaming Agents	0.001-0.1	0.001-0.01
Anti-wear Agents	0.001-5	0.001-1.5
Seal Swell Agents	0.1-8	0.1-4
Friction Modifiers	0.01-3	0.01-1.5
Lubricating Base Oil	Balance	Balance

**[0057]** When other additives are employed, it may be desirable, although not necessary, to prepare additive concentrates comprising concentrated solutions or dispersions of the subject additives of this invention together with one or more of said other additives (said concentrate when constituting an additive mixture being referred to herein as an additive-package) whereby several additives can be added simultaneously to the base oil to form the lubricating oil composition. Dissolution of the additive concentrate into the lubricating oil can be facilitated by solvents and by mixing accompanied by mild heating, but this is not essential.

**[0058]** The concentrate or additive-package will typically be formulated to contain the additives in proper amounts to provide the desired concentration in the final formulation when the additive-package is combined with a predetermined amount of base lubricant. Thus, the subject additives of the present invention can be added to small amounts of base oil or other compatible solvents along with other desirable additives to form additive-packages containing active ingredients in collective amounts of, typically, from about 2.5 to about 90 percent, preferably from about 15 to about 75 percent, and more preferably from about 25 percent to about 60 percent by weight additives in the appropriate proportions with the remainder being base oil. The final formulations can typically employ about 1 to 20 weight percent of the additive-package with the remainder being base oil.

**[0059]** All of the weight percentages expressed herein (unless otherwise indicated) are based on the active ingredient (AI) content of the additive, and/or upon the total weight of any additive-package, or formulation, which will be the sum of the AI weight of each additive plus the weight of total oil or diluent.

**[0060]** In general, the lubricant compositions contain the additives in a concentration ranging from about 0.05 to about 30 weight percent. A concentration range for the additives ranging from about 0.1 to about 10 weight percent based on the total weight of the oil composition is preferred. A more preferred concentration range is from about 0.2 to about 5 weight percent. Oil concentrates of the additives can contain from about 1 to about 75 weight percent of the additive reaction product in a carrier or diluent oil of lubricating oil viscosity.

**[0061]** In general, the additives are used in a variety of lubricating oil base stocks. The lubricating oil base stock is any natural or synthetic lubricating oil base stock fraction having a kinematic viscosity at 100°C of about 2 to about 200 cSt, more preferably about 3 to about 150 cSt, and most preferably about 3 to about 100 cSt. The lubricating oil base stock can be derived from natural lubricating oils, synthetic lubricating oils or mixtures thereof. Suitable lubricating oil base stocks include base stocks obtained by isomerization of synthetic wax and wax, as well as hydrocracked base stocks produced by hydrocracking (rather than solvent extracting) the aromatic and polar components of the crude. Natural lubricating oils include animal oils, such as lard oil, vegetable oils (e.g., canola oils, castor oils, sunflower oils), petroleum oils, mineral oils, and oils derived from coal or shale.

**[0062]** Synthetic oils include hydrocarbon oils and halo-substituted hydrocarbon oils, such as polymerized and interpolymerized olefins, gas-to-liquids prepared by Fischer-Tropsch technology, alkylbenzenes, polyphenyls, alkylated diphenyl ethers, alkylated diphenyl sulfides, as well as their derivatives, analogs, homologs, and the like. Synthetic lubricating oils also include alkylene oxide polymers, interpolymers, copolymers, and derivatives thereof, wherein the terminal hydroxyl groups have been modified by esterification, etherification, etc.

[0063] Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids -with a variety of alcohols. Esters useful as synthetic oils also include those made from C<sub>5</sub> to C<sub>12</sub> monocarboxylic acids and polyols and polyol ethers. Other esters useful as synthetic oils include those made from copolymers of  $\alpha$ -olefins and dicarboxylic acids that are esterified with short or medium chain length alcohols. The following are exemplary of such additives and are commercially available from Akzo Nobel Chemicals SpA: Ketjenlubes 115, 135, 165, 1300, 2300, 2700, 305, 445, 502, 522, and 6300, among others.

[0064] Silicon-based oils, such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy- siloxane oils and silicate oils, comprise another useful class of synthetic lubricating oils.

[0065] Other synthetic lubricating oils include liquid esters of phosphorus-containing acids, polymeric tetrahydrofurans, poly  $\alpha$ -olefins, and the like.

[0066] The lubricating oil may be derived from unrefined, refined, re-refined oils, or mixtures thereof. Unrefined oils are obtained directly from a natural source or synthetic source (e.g., coal, shale, or tar and bitumen) without further purification or treatment. Examples of unrefined oils include a shale oil obtained directly from a retorting operation, a petroleum oil obtained directly from distillation, or an ester oil obtained directly from an esterification process, each of which is then used without further treatment. Refined oils are similar to unrefined oils, except that refined oils have been treated in one or more purification steps to improve one or more properties. Suitable purification techniques include distillation, hydrotreating, dewaxing, solvent extraction, acid or base extraction, filtration, percolation, and the like, all of which are well-known to those skilled in the art. Re-refined oils are obtained by treating refined oils in processes similar to those used to obtain the refined oils. These re-refined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for removal of spent additives and oil breakdown products.

[0067] Lubricating oil base stocks derived from the hydroisomerization of wax may also be used, either alone or in combination with the aforesaid natural and/or synthetic base stocks. Such wax isomerate oil is produced by the hydroisomerization of natural or synthetic waxes or mixtures thereof over a hydroisomerization catalyst. Natural waxes are typically the slack waxes recovered by the solvent dewaxing of mineral oils; synthetic waxes are typically the wax produced by the Fischer-Tropsch process. The resulting isomerate product is typically subjected to solvent dewaxing and fractionation to recover various fractions having a specific viscosity range. Wax isomerate is also characterized by possessing very high viscosity indices, generally having a VI of at least 130, preferably at least 135 or higher and, following dewaxing, a pour point of about -20°C or lower.

[0068] The additives are especially useful as components in many different lubricating oil compositions. The additives can be included in a variety of oils with lubricating viscosity, including natural and synthetic lubricating oils and mixtures thereof. The additives can be included in crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines. The compositions can also be used in gas engine lubricants, turbine lubricants, automatic transmission fluids, gear lubricants, compressor lubricants, metal-working lubricants, hydraulic fluids, and other lubricating oil and grease compositions. The additives can also be used in motor fuel compositions. The advantages and the important features of the present invention will be more apparent from the following examples.

## EXAMPLES

[0069] The following examples demonstrate the efficacy of the substituted 1,3-dithiolane-2-thiones as lubricant additives, alone and in synergistic combination with phosphorus-containing additives, such as zinc dialkyldithiophosphate. In addition, they show no harm in corrosion testing.

### Examples 6-7

#### 45 1,3-Dithiolane-2-thione Derivative of Epoxidized 2-Ethylhexyl Tallate

[0070] A 1000 mL 4-neck flask was charged with 22.2 grams of sodium hydroxide and 38 grams of water. The material was stirred, and then 428.5 grams of 1-butanol was added, and the mixture was stirred for 15 minutes. Carbon disulfide, 38.1 grams, was added at 26°C over 30 minutes. The mixture was stirred for 30 minutes more, and then 170.2 grams of Drapex® 4.4 epoxidized 2-ethylhexyl tallate was added dropwise over 45 minutes. The reaction mixture was stirred at 50°C for two hours, and then at 70°C for three hours. The reaction mixture was cooled to room temperature, and brought to pH 8 by addition of acetic acid. Water was added (100 mL), and the mixture was stirred for 15 minutes. The reaction mass was transferred to a separatory funnel and the aqueous phase was removed. Xylenes (450 mL) were added, and the product was washed twice with 200 mL portions of water. The product was dried over sodium sulfate and magnesium sulfate and then filtered. Volatiles were removed by rotary evaporation to give 186.6 grams of a clear yellow liquid.

**Examples 8-9****1,3-Dithiolane-2-thione Derivative of Epoxidized 2-Ethylhexyl Tallate**

5 [0071] A 1000 mL 4-neck flask (equipped with an overhead stirrer, a condenser vented to a caustic scrubber, an addition runnel, and a thermocouple/nitrogen inlet) was charged with 21.0 grams of sodium hydroxide and 40 grams of water. The material was stirred, and then 431 grams of 1-butanol was added and the mixture was stirred for five minutes. Carbon disulfide, 83.04 grams, was added at 29-32°C over 50 minutes. The mixture was stirred for 15 minutes more, and then 168.8 grams of Drapex 4.4 epoxidized 2-ethylhexyl tallate (Crompton Corp.) was added dropwise over 24 minutes. The reaction mixture was heated to 50°C, and stirred at 50°C for two hours. The temperature was increased to 70°C, and the reaction was stirred for an additional three hours. The reaction mixture was cooled to 65°C and 30 mL of glacial acetic acid was added. Water was added (100 mL). The mixture was stirred for 40 minutes. The reaction mass was transferred to a separatory funnel and the aqueous phase was removed. Xylenes (450 mL) were added, and the product was washed four times with 100 mL portions of water. The product was dried over magnesium sulfate, and then 10 filtered through a Buchner funnel with Whatman #4 paper, and then through diatomaceous earth. Volatiles and solvent were removed by rotary evaporation to give a clear 15 yellow liquid.

**Anti-Wear Four-Ball Testing**

20 [0072] The anti-wear properties of the 1,3-dithiolane-2-thiones in a fully formulated American Petroleum Institute (API Group II lubricating oil were determined in the Four-Ball Wear Test under the ASTM D 4172 test conditions. The testing for these examples was done on a Falex Variable Drive Four-Ball Wear Test Machine. Four balls are arranged in an equilateral tetrahedron. The lower three balls are clamped securely in a test cup filled with lubricant and the upper ball 25 is held by a chuck that is motor-driven. The upper ball rotates against the fixed lower balls. Load is applied in an upward direction through a weigh/lever arm system. Loading is through a continuously variable pneumatic loading system. Heaters allow operation at elevated oil temperatures. The three stationary steel balls are immersed in 10 milliliters of sample to be tested, and the fourth steel ball is rotated on top of the three stationary balls in "point-to-point contact." The machine is operated for one hour at 75°C with a load of 40 kilograms and a rotational speed of 1,200 revolutions 30 per minute. The fully formulated lubricating oil contained all the additives typically found in a motor oil (with different anti-wear agents as noted in TABLE 2) as well as 0.5 wt.% cumene hydroperoxide to help simulate the environment within a running engine.

35 [0073] The additives were tested for effectiveness in a motor oil formulation and compared to identical formulations with and without any zinc dialkyldithiophosphate. It will be apparent from examination of the data that the use of these hydroxy ester additives in combination with phosphorus-containing additives offers synergistic improvement in performance over either type of additive alone.

**Anti-wear Cameron-Plint TE77 High Frequency Friction Machine Testing**

40 [0074] The anti-wear properties of the additives of this invention in a fully formulated API Group TI lubricating oil were determined in the Cameron-Plint TE77 High Frequency Friction Machine Test. The specimen parts (6 mm diameter AISI 52100 steel ball of  $800 \pm 20$  kg/mm<sup>2</sup> hardness and hardened ground NSOH BOI gauge plate of RC 60/0.4 micron) were rinsed and then sonicated for 15 minutes with technical grade hexanes. This procedure was repeated with isopropyl alcohol. The specimens were dried with nitrogen and set into the TE77. The oil bath was filled with 10 mL of sample. 45 The test was run at a 30 Hertz frequency, 100 Newton load, 2.35 mm amplitude. The test starts with the specimens and oil at room temperature. Immediately, the temperature was ramped over 15 minutes to 50°C, where it dwelled for 15 minutes. The temperature was then ramped over 15 minutes to 100°C, where it dwelled for 45 minutes. A third temperature ramp over 15 minutes to 150°C was followed by a final dwell at 150°C for 15 minutes. The total length of the test was 50 2 hours. At the end of test, the wear scar diameter on the 6 mm ball was measured using a Leica StereoZoom6® Stereomicroscope and a Mitutoyo 164 series Digimatic Head. The fully formulated lubricating oils tested contained 1 weight % cumene hydroperoxide to help simulate the environment within a running engine.

55 [0075] The additives were tested for effectiveness in motor oil formulations and compared to identical formulations with and without any zinc dialkyldithiophosphate. In TABLE 2 the numerical value of the test results (Wear Scar Diameter, mm) decreases with an increase in effectiveness.

[0076] Also determined was the maximum depth of the wear scar on the plate. This is measured using a profilometer (mm). The number in parentheses (#x), is the number of repeat experiments used for the average value.

TABLE2 Anti-Wear Test						
Example	Anti-Wear Chemical Name	Four-Ball		Cameron Plint		
		Ave. of Scar (mm)	No. of Repitions	Ave. Ball Scars (mm)	Ave. Plate Scars Depth (IJ.rn)	No. of Repetitions
A	ZDDP 1% (Comparative)	0.481	49	0.424	1.79	43
B	No Anti-wear (Comparative)	0.794	40	0.754	15.54	52
6	1,3-Dithiolane-2-thione derivative of epoxidized	0.440	11	0.785	11.669	2
7	1,3-Dithiolane-2-thione derivative of epoxidized 2-ethylhexyl tallate) 0.50%	0.385	2	0.361	2.129	2
8	1,3-Dithiolane-2-thione derivative of epoxidized	0.475	2	0.740	7.975	2
9	1,3-Dithiolane-2-thione derivative of epoxidized 2-ethylhexyl tallate)	0.405	2	0.448	2.115	2

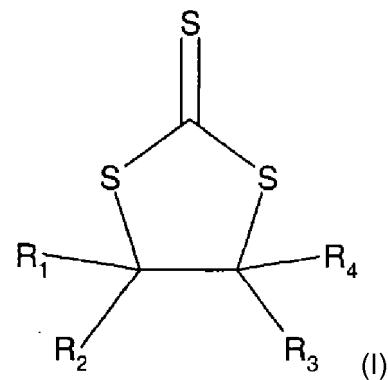
### Lead and Copper Corrosion Testing

[0077] In TABLE 3 are the results of a Cummins bench test for measuring the degree of Cu and Pb corrosion of an oil formulation. The Cummins bench test is part of the API CH-4 category for diesel engine oils. Four metal coupons (25.4 mm squares) of pure lead, copper, tin, and phosphor-bronze are immersed in 100 mL of oil at 121°C with air bubbling through (5 L/hr) for 168 hours. The used oil is analyzed for metals and the copper sample is examined for discoloration. The limits for API CH-4 are 20 ppm Cu, 120 ppm Pb, 50 ppm Sn in used oil and 3 max for the ASTM D 130 rating of the copper square. Additives were blended into a fully formulated SAE 15-W40 oil with ILSAC GF-2 credentials. In the first row of TABLE 3 are data generated on the SAE 15W-40 oil without any top treat of other additives. The substituted 1,3-dithiolane-2-thione did very well on Pb corrosion with passing results.

TABLE 3 ASTM D 5968 Corrosion Bench Test of Engine Oil at 121°C					
Additive (in Rotella T SAE 15W-40)		Weight % Additive	Copper (ppm)	Lead (ppm)	ASTM D130
Reference		0.0	7	11.9	1b
1,3-Dithiolane-2-thione derivative of epoxidized 2-ethylhexyl tallate		1.0	9.5	3.0	1b
1,3-Dithiolane-2-thione derivative of epoxidized 2-ethylhexyl tallate		1.0	7	3.3	1b

### Claims

1. Use of at least one substituted 1,3-dithiolane-2-thione of formula (I),



2. Verwendung nach Anspruch 1, ferner umfassend mindestens ein phosphorhaltiges Additiv.

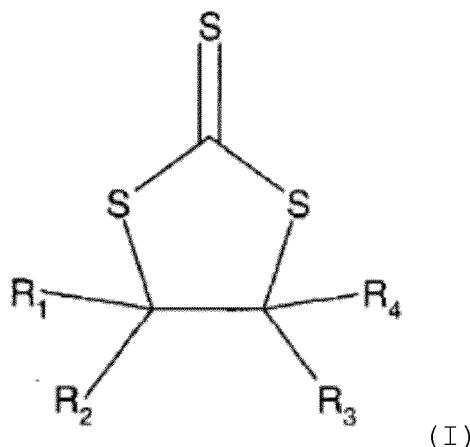
3. Verwendung nach Anspruch 2, wobei es sich bei mindestens einem phosphorhaltigen Additiv um ein Dihydrocarbyldithiophosphat handelt.

5

**Revendications**

1. Utilisation d'au moins une 1,3-dithiolane-2-thione substituée de formule (I),

10



R<sub>1</sub> étant  $(CH_2)_pCO_2R_5$  et

R<sub>5</sub> étant choisi dans le groupe constitué par hydrocarbyle saturé à chaîne substituée, p étant de 1 à 50 et

30 R<sub>2</sub>, R<sub>3</sub> et R<sub>4</sub> étant indépendamment choisis dans le groupe constitué par hydrogène et alkyle, ledit alkyle étant non substitué ou substitué par 1,3-dithiolane-2-thione ; destiné à l'amélioration des propriétés anti-corrosion d'un lubrifiant.

2. Utilisation selon la revendication 1 comprenant en outre au moins un additif contenant du phosphore.

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3. Utilisation selon la revendication 2, au moins un additif contenant du phosphore étant un dithiophosphate de dihydrocarbyle.

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**REFERENCES CITED IN THE DESCRIPTION**

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